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June 11, 1992

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Sincerely,

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SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

Form Approved OMB No 0704 0188

1a REPORT SECURITY CLASSIFICATION: Unclassified	1b. RESTRICTIVE MARKINGS
2a SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT: List attached
2b DECLASSIFICATION/DOWNGRADING SCHEDULE	
4 PERFORMING ORGANIZATION REPORT NUMBER(S): 13	5. MONITORING ORGANIZATION REPORT NUMBER(S)
6a NAME OF PERFORMING ORGANIZATION: Purdue University; 6b OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION: Office of Naval Research
6c. ADDRESS (City, State, and ZIP Code): West Lafayette, IN 47907	7b. ADDRESS (City, State, and ZIP Code): Department of the Navy, Arlington, VA 22217
8a NAME OF FUNDING/SPONSORING ORGANIZATION: Office of Naval Research; 8b OFFICE SYMBOL (If applicable)	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER: N00014-89-J-1128
8c ADDRESS (City, State, and ZIP Code): 800 North Quincy Street, Arlington, VA 22217-5000	10. SOURCE OF FUNDING NUMBERS: PROGRAM ELEMENT NO. / PROJECT NO. / TASK NO. / WORK UNIT ACCESSION NO

11 TITLE (Include Security Classification) Organoboranes. 55. An Improved Procedure for the Conversion of Representative Achiral and Chiral Monoalkyl-, [*E*]- and [*Z*]-Alkenyl-, and Arylboronates into the Corresponding Organyldichloroboranes

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13a TYPE OF REPORT	13b TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Technical	FROM _____ TO _____	June 9, 1992	18

16 SUPPLEMENTARY NOTATION: accepted in *Organometallics*

17. COSATI CODES		
FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number): Chiral monoalkyldichloroboranes, high enantiomeric purity, [*E*]- and [*Z*]-alkenyldichloroboranes, high isomeric purity, aryldichloroboranes

19 ABSTRACT (Continue on reverse if necessary and identify by block number)

Chiral alkylboronates of essentially 100% enantiomeric purity prepared by asymmetric hydroboration of readily available prochiral olefins were effectively converted into the corresponding chiral monoalkyldichloroboranes by treatment with boron trichloride (1 M solution in dichloromethane) in the presence of a catalytic amount of anhydrous ferric chloride (3 mole %). This procedure works equally well for the conversion of [*E*]- and [*Z*]-alkenylboronates, phenylboronates and *tert*-butylboronates into the corresponding dichloroboranes respectively.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☐ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS	Unclassified
22a NAME OF RESPONSIBLE INDIVIDUAL: Herbert C. Brown	22b TELEPHONE (Include Area Code): (317) 494-5316; 22c. OFFICE SYMBOL

DD Form 1473, JUN 86 Previous editions are obsolete. SECURITY CLASSIFICATION OF THIS PAGE

OFFICE OF NAVAL RESEARCH

Contract N00014-89-J-1128

R&T Code 4135011---08

Technical Report No. 13

Organoboranes. 55. An Improved Procedure for the Conversion of Representative Achiral and Chiral Monoalkyl-, (E)- and (Z)-Alkenyl-, and Arylboronates into the Corresponding Organyldichloroboranes

by

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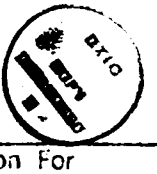
Accepted for Publication

in

Organometallics

June 11, 1992



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Organoboranes. 55. An Improved Procedure for the Conversion of Representative Achiral and Chiral Monoalkyl-, (*E*)- and (*Z*)-1-Alkenyl-, and Arylboronates into the Corresponding Organyldichloroboranes.

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Diethyl alkylboronates, $R^*B(OEt)_2$, of essentially 100% enantiomeric purity, prepared by asymmetric hydroboration of readily available prochiral alkenes, were effectively converted into the corresponding chiral monoalkyldichloroboranes, R^*BCl_2, by treatment with boron trichloride (1M solution in dichloromethane) in the presence of a catalytic amount of anhydrous ferric chloride (3 mole %). This reaction is quite general and proceeds well without detectable racemization, and is applicable to essentially optically pure boronic esters of widely varied structural requirements. The reaction is also applicable to achiral boronates, such as 1-hexyl-, and hindered alkyl, such as *tert*-butyl. It is also applicable to the conversion of (*E*)- and (*Z*)-1-hexenylboronates, representative of the 1-alkenyl derivatives, and to phenyl-, representative of aryl derivatives. Consequently, this procedure appears to be broadly applicable to the conversion of organylboronates, $RB(OR')_2$, into the corresponding organyldichloroboranes, $RBCl_2$.

Introduction

Organoboranes have proven to be highly valuable intermediates for organic syntheses, due to their high reactivity, ease of preparation, and exceptional synthetic utility.[2] Among these organoboranes, the organyldichloroboranes, $RBCl_2$, are especially valuable because of easy accessibility, exceptionally high reactivity, and the especially economical utilization of the organic group introduced.[3] The utility of organyldichloroboranes is well documented in the literature.[3,4] The chiral organyldichloroboranes, R^*BCl_2, derived from chiral alkylboronic esters, are assuming a major importance in our efforts to develop a general synthesis of enantiomerically pure compounds.[5] Recently chiral alkyldichloroboranes have been used as a catalyst in asymmetric Diels-Alder reactions.[6] Chiral alkylboronic esters are exceptionally promising intermediates for carbon-carbon bond forming reactions.[7] These reactions are especially valuable for chiral syntheses proceeding through organoborane intermediates. Yet it is often highly desirable to convert the comparatively unreactive boron-oxygen bonds in these intermediates to the highly reactive boron-hydrogen or boron-chlorine bonds.[5] The successful achievement of this objective would greatly extend both the range of the versatility and the diversity of chiral organoborane chemistry. We have already achieved the quantitative conversion of the boron-oxygen bonds in chiral boronic esters to boron-hydrogen bonds in chiral monoalkylborohydrides.[8]

Several methods have been reported in the literature for the preparation of various organyldichloroboranes.[9-15] Many of them involve the preparation of arylhaloboranes. In general, these compounds have been prepared by the interaction of either gaseous boron trichloride or boron trifluoride with alumina[9] in the form of its slurry with aromatic hydrocarbons, or with organometallic compounds, such as boronic esters,[10a] boronic anhydrides,[10b] triarylboroxines,[10c] diarylmercury,[11] tetraaryltin[12] and vinyltin.[12d] The high temperature reaction of boron trichloride with benzene catalysed by palladium[13] is known to

give phenyldichloroborane. Grignard reagents[14], zinc aryls[15] and phosphorus pentachloride[15b,c,d] have been utilized for the preparation of aryldichloroboranes. Among these methods, some involve the use of either gaseous boron trichloride or boron trifluoride condensed at –78 °C, and some involve the use of gaseous boron trifluoride in boiling carbon tetrachloride,[12a] dichloromethane[12a] or benzene.[12b]

Several methods are available in the literature for proceeding from boronic esters.[5,10a,15b,c,d] The first method reported in 1956 by Lappert *et. al.*[10a] involves the interaction of neat boronic esters, $RB(OR')_2$ with gaseous boron trichloride at –78 °C in the presence of a catalytic amount of ferric chloride to give the corresponding organyldichloroboranes, $RBCl_2$, in good yields (eq 1, 2). In this reference only two examples were studied under neat conditions. The second method recently reported from our group [5]

$$RB(OR')_2 + 2BCl_3 \longrightarrow RBCl_2 + 2BCl_2OR' \quad (1)$$

$$3BCl_2OR' \xrightarrow{FeCl_3} 3R'Cl + BCl_3 + B_2O_3 \quad (2)$$

R = *n*-butyl, phenyl
R' = *n*-butyl

involves treatment of boronic esters with LAH to give the monoalkylborohydrides (eq 3).[8] This, upon treatment with 3 equiv. of HCl in dimethyl sulphide, yields the organyldichloroborane-dimethyl sulphide complexes in excellent yields (eq 4). This two-step procedure involves the separation of dialkoxyalane, which in some instances does not precipitate cleanly, especially in the case of acyclic boronic esters.

(3)

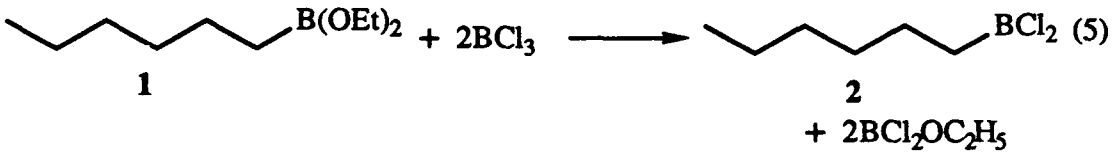
$$R^*BH_3Li \xrightarrow{3HCl \text{ in } SMe_2} R^*BCl_2{\cdot}SMe_2 + LiCl + 3H_2\uparrow \quad (4)$$

Therefore, as a part of our ongoing program in this area and the non-availability of a convenient general procedure, we undertook to develop such a general procedure, applicable to the preparation of a wide variety of organyldichloroboranes from the corresponding boronic esters. Here we are reporting an improved procedure for the conversion of chiral alkylboronic esters to highly reactive chiral monoalkyldichloroboranes in very high enantiomeric purities. This procedure has advantages over currently available procedures. Its applicability has also been demonstrated for the preparation of *(E)*- and *(Z)*-1-alkenyl-, and phenyldichloroborane as a representative aryl derivative from the respective boronic esters. This procedure is also effective for the conversion of the sterically hindered *tert*-butylboronic ester to the corresponding *tert*-butyldichloroborane. The reaction appears to be general and provides a simple economical approach for the synthesis of various types of organyldichloroboranes in satisfactory yields.

Results and Discussion

The earlier procedure[10a] for the preparation of organyldichloroboranes involves the interaction of neat boronic esters with two equivalents of gaseous boron trichloride in presence of a catalytic amount of ferric chloride at low temperature (–78 °C). Under these conditions, only $PhB(OBu^n)_2$ and n-$BuB(OBu^n)_2$ have been converted to the corresponding $PhBCl_2$ and n-$BuBCl_2$ respectively. In order to simplify this promising reaction to obtain clean organyldichloroboranes, we first examined the reaction of diethyl *n*-hexylboronate[16] (**1**) with commercially available boron trichloride in the presence of a catalytic amount of ferric chloride at 0 °C monitoring the reaction progress by ^{11}B NMR. The ^{11}B NMR study of the reaction mixture, after stirring at 0 °C and 25 °C for 1h each, showed the complete disappearance of the boronic ester peak at δ 30 and the appearance of the *n*-hexyldichloroborane[17] peak at δ 63, along with peaks at δ 46 and δ 26, indicative of BCl_3 and B_2O_3 respectively (eq 5, for

decomposition[18] of $BCl_2OC_2H_5$ see eq 2). The decomposition of dichloroborinate,Cl_2BOR' to R'Cl, BCl_3 and B_2O_3 under the influence of catalytic quantities of ferric chloride is known.[18] After removal of volatile matter under reduced pressure (20 mm Hg), the resulting residue was extracted with dichloromethane. Removal of solvent under reduced pressure

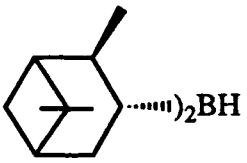


yields *n*-hexyldichloroborane[17] in 80% yield. It was purified by distillation under reduced pressure, bp 100 °C/100 mm Hg (lit.[17] bp 102-104 °C /100 mm Hg). This yield is comparable to that realized by the earlier procedure.[10a] After establishing the most suitable reaction conditions, we examined various cyclic and acyclic ester derivatives of boronic acids, such as dimethyl-, diethyl- and ethylene glycol, in order to find out the most suitable ester derivative under these reaction conditions. Among these, dimethyl and diethyl derivatives of the boronic acid gave comparable favorable results, whereas in the case of the cyclic ester derivatives the separation of product becomes difficult. Hence, for our study, we adopted the diethyl ester derivatives of boronic acids readily prepared from the corresponding boronic acids and absolute alcohol.[16]

Having established both suitable reaction conditions and a favorable ester derivative, we turned our attention towards extending the applicability of this improved procedure to the conversion of chiral alkylboronic esters to the corresponding chiral alkyldichloroboranes. Similarly, we applied this procedure to the conversion of *(E)*- and *(Z)*- 1-alkenylboronic esters to the *(E)*- and *(Z)*-1-alkenyldichloroboranes respectively, and also to the conversion of phenylboronic ester (as a representative aryl derivative) to phenyldichloroborane. Conversion

of *tert*-butylboronic ester (as a representative hindered derivative) to *tert*-butyldichloroborane was also examined.

Preparation of Chiral Monoalkyl-, *(E)*- and *(Z)*-1-Alkenyl-, Phenyl- and *tert*-Butylboronic esters: The optically active organoborane intermediates, chiral monoalkylboronic esters, $R^*B(OEt)_2$ required for this study, were prepared by asymmetric hydroboration of an appropriate prochiral olefin with either (+)-diisopinocampheylborane, $^d Ipc_2BH$ (**3**), (≥99% ee)[19] or (+)-monoisopinocampheylborane, $^d IpcBH_2$ (**4**), (≥99% ee),[20] both easily prepared from (+)-α -pinene. Thus, asymmetric hydroboration of *cis*-2-butene with $^d Ipc_2BH$ (**3**) gave trialkylborane,[21] which upon treatment with 1.8 equivalents of



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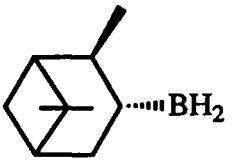

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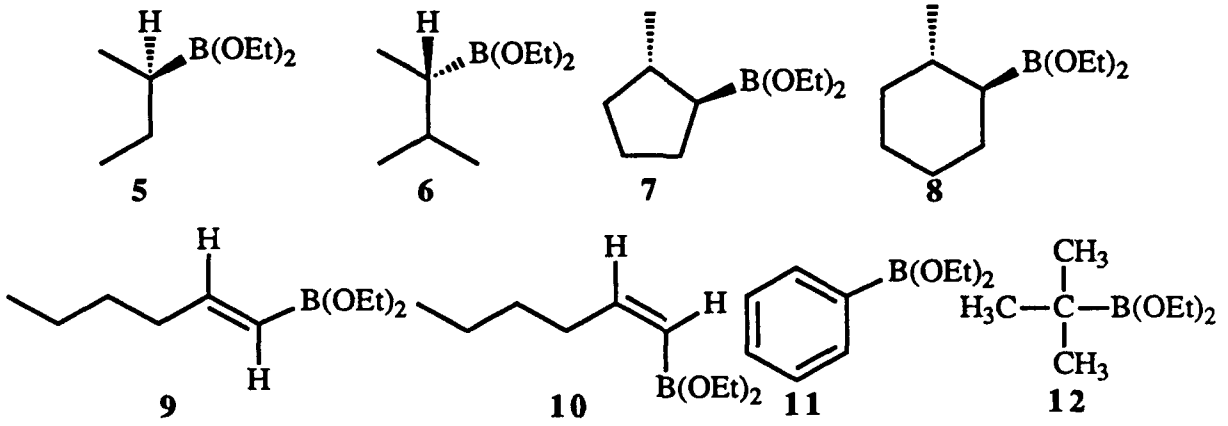
benzaldehyde resulted in selective facile elimination of the chiral auxiliary, providing the corresponding boronic ester. This on extraction with 3N NaOH followed by acidification with 3N HCl provided (*R*)-2-butylboronic acid in very high enantiomeric purity.[21d] The chiral diethyl (*R*)-2-butylboronate (**5**) was then prepared by esterification of (*R*)-2-butylboronic acid with absolute alcohol.[16] Similarly, the asymmetric hydroboration of prochiral olefins with $^d IpcBH_2$ (**4**), followed by crystallization of the intermediates gave optically pure isopinocampheylalkylborane (≥99% ee).[20, 21] This on treatment with acetaldehyde under mild conditions yielded the corresponding boronic esters in very high enantiomeric purity after the elimination of chiral auxiliary. Optically active diethyl boronates (**6-8**) were then prepared by esterification of the corresponding boronic acids with absolute alcohol.[16] By employing this procedure (*S*)-diethyl (3-methyl-2-butyl)boronate (**6**), (*1S, 2S*)-diethyl *trans*-(2-

methylcyclopentyl)boronate (**7**) and (*1S, 2S*)-diethyl *trans*-(2-methylcyclohexyl)boronate (**8**) have been obtained in high enantiomeric purities.[22]

Diethyl (*E*)-1-hexenylboronate (**9**) was prepared, as previously described in high chemical yield and high stereochemical purity, by the hydroboration of 1-hexyne with $BHBr_2{\cdot}SMe_2$ [23] followed by the treatment with absolute alcohol.



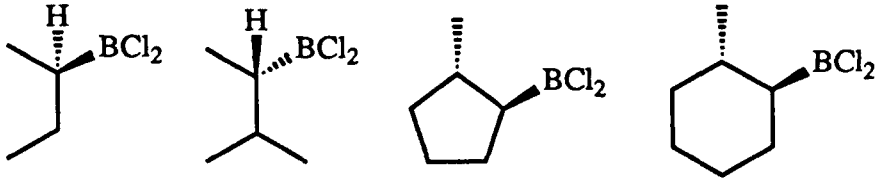
Diethyl (*Z*)-1-hexenylboronate (**10**) was prepared in high stereochemical purity according to the reported procedure.[24] The hydroboration of 1-bromo-1-hexyne with $BHBr_2{\cdot}SMe_2$, followed by treatment with 2-propanol gave diisopropyl (*Z*)-(1-bromo-1-hexenyl)boronate, which upon treatment with potassium triisopropoxyborohydride (KIPBH), afforded diisopropyl (*Z*)-1-hexenylboronate. It was then converted into the diethyl (*Z*)-1-hexenylboronate (**10**) by trans esterification with ethanol. Diethyl phenylboronate (**11**) was prepared by esterification of readily available phenylboronic acid with absolute alcohol.[16] Similarly diethyl *tert*-butylboronate (**12**) was prepared according to the known procedure.[25]

Preparation of Chiral Alkyldichloroboranes, (*E*)-and (*Z*)-1-Alkenyldichloroboranes and Phenyldichloroborane. After studying the conversion of *n*-hexylboronic ester (**1**) to *n*-hexyldichloroborane (**2**) (eq 5), and having all requisite

boronic esters (**5-12**) in hand, we examined their conversion to the respective dichloroboranes (**13-20**) as follows. The reaction of chiral alkylboronic esters (**5-8**) with 2 equivalents of 1M solution of boron trichloride in dichloromethane (available from Aldrich Chemical Co.), in presence of a catalytic amount of anhydrous ferric chloride (3 mole %) at 0 °C and 25 °C for 1h each, showed the formation of the corresponding chiral alkyldichloroboranes, R^*BCl_2 based on the observation made by the ^{11}B NMR study. The ^{11}B NMR spectrum of the reaction mixture showed disappearance of the boronic ester peak at δ 30 and the appearance of peaks at δ 46 and δ 26, indicative of BCl_3 and B_2O_3 respectively (eq 6; for decomposition[18] of $BCl_2OC_2H_5$, see eq 2). The volatile matter was removed under reduced pressure and the

$$\underset{\textbf{5-8}}{R^*B(OEt)_2} + 2BCl_3 \longrightarrow \underset{\textbf{13-16}}{R^*BCl_2} + 2BCl_2OC_2H_5 \quad (6)$$

resulting residue was extracted with fresh dichloromethane. Removal of the solvent gave the desired alkyldichloroborane, which was purified by distillation under vacuum.



13 **14** **15** **16**

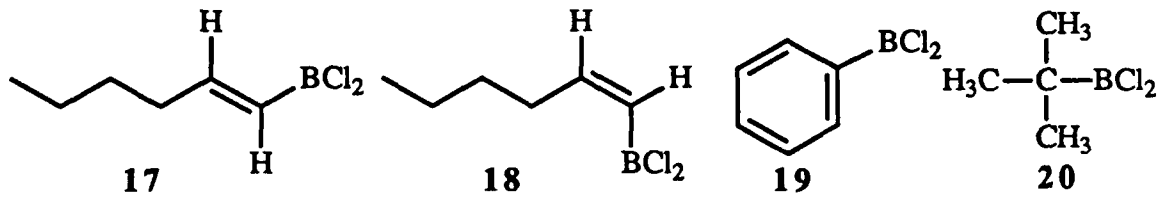
By using this procedure, the efficient conversions of (*R*)-diethyl-2-butylboronate (**5**) to (*R*)-2-butyldichloroborane (**13**), (*S*)-diethyl-(3-methyl-2-butyl)boronate (**6**) to (*S*)-(3-methyl-2-butyl)*dichloroborane* (**14**), (*1S, 2S*)-diethyl *trans*-(2-methylcyclopentyl)boronate (**7**) to (*1S, 2S*)-*trans*-(2-methylcyclopentyl)dichloroborane (**15**) and (*1S, 2S*)-diethyl *trans* -(2-methylcyclohexyl)boronate (**8**) to (1*S*, 2*S*)-*trans*-(2-methylcyclohexyl)dichloroborane (**16**) have been successfully achieved. The isolated yields realized are in the range of 60-65% (Table I).

Under these experimental conditions the conversion of chiral monoalkylboronic esters to the corresponding chiral alkyldichloroboranes occured with the complete maintenance of stereochemical integrity. All chiral alkyldichloroboranes (**13-16**) were obtained in very high enantiomeric purity.[22]

Further, in order to explore the utility of this procedure, diethyl (*E*)-1-hexenylboronate (**9**) and diethyl (*Z*)-1-hexenylboronate (**10**) were subjected to these improved reaction conditions and the reaction results examined. Thus (*E*)-1-hexenylboronic ester (**9**) was regioselectively converted to (*E*)-1-hexenyldichloroborane (**17**) in 75% isolated yield, bp 104 °C (100 mm Hg) (lit.[26] bp 66-68 °C/18 mm Hg) (eq 7, for decomposition[18] of $BCl_2OC_2H_5$ see eq 2).

$$\underset{\textbf{9-12}}{RB(OEt)_2} + 2BCl_3 \longrightarrow \underset{\textbf{17-20}}{RBCl_2} + 2BCl_2OC_2H_5 \quad (7)$$

Since the literature survey reveals that there is no method for the preparation of (*Z*)-1-alkenyldichloroboranes, we decided to test our improved procedure for this application. Thus diethyl (*Z*)-1-hexenylboronate (**10**) was effectively and successfully converted to (*Z*)-1-hexenyldichloroborane (**18**) in 72% isolated yield, bp 104 °C (102 mm Hg) (eq 7). The stereochemical purities of (**17**) and (**18**) were checked on high resolution ^1H NMR. To the best of our knowledge, this is the first, simple and efficient procedure for the preparation of (*Z*)-alkenyldichloroboranes.



Further, this procedure works equally well for the conversion of phenylboronic ester (**11**) to phenyldichloroborane (**19**) in 67% isolated yield, bp 66 °C (11 mm Hg) (lit.[10b] bp 66-66.5 °C(11mm Hg) (eq 5). Additionally, the successful exploitation of this procedure was shown for the conversion of the bulky *tert*-butyl boronic ester (**12**) to *tert*-butyldichloroborane (**20**) in 65% isolated yield, bp 86 °C/ 744 mm Hg, (lit.[27] bp 88 °C/ 744 mm Hg) (Table II).

We decided to examine the applicability of this reaction for the conversion of boronic acids into the desired borondichlorides. However, when phenylboronic acid, $PhB(OH)_2$ was allowed to react with boron trichloride under such reaction conditions, only 16% of the desired product, $PhBCl_2$ was formed, with the recovery of 84% of starting boronic acid. This result reveals that this procedure is not suitable for the conversion of boronic acids to dichloroboranes, eventhough the procedure works very well for converting boronic esters to the corresponding dichloroboranes. The structures of these dichloroboranes (**13-20**) were confirmed on the basis of ^{11}B NMR, ^{1}H NMR, ^{13}C NMR and literature data. The chemical purity of these dichloroboranes (**13-20**) was checked by ethanolysis and analysis of the resulting boronic esters by ^{1}H NMR.[20b]

Conclusions

The procedure developed in this study provides a simple, convenient and efficient approach for the preparation of chiral monoalkyldichloroboranes, R^*BCl_2, from the respective chiral monoalkylboronic esters, $R^*B(OEt)_2$, in very high enantiomeric purity. Previously there has been no procedure available for the preparation of (*Z*)-alkenyldichloroboranes. Now their preparation is readily achievable by this procedure. Similarly, this procedure makes possible the ready preparation of aryldichloroboranes from the corresponding boronic esters. From the above results and discussion, it is clear that this procedure works well for the conversion of essentially all types of boronic esters to give the corresponding organyldichloroboranes. In

view of the growing utility of the $RBCl_2$ compounds in organic synthesis, the present study should encourage further research in this area, using the RBX_2 compounds as a synthon.

Experimental Section

All glassware used for the experiments were dried in an oven at 140 °C for several hours, assembled hot, and cooled under a stream of nitrogen. All operations were carried out under an inert atmosphere (N_2). ^{11}B NMR,^1H NMR, and ^{13}C NMR spectra were recorded on a Varian Gemini-300 spectrometer. The ^{11}B NMR chemical shifts are with reference to BF_3:OEt_2 (δ 0) and the resonance values upfield from the standard are assigned negative signs. For ^1H NMR and ^{13}C NMR the chemical shifts are in δ values relative to that of TMS. Capillary GC analyses were carried out with a Hewlett-Packard 5890 chromatograph fitted with 15-m Supelcowax / 30-m SPB-5 columns.

Materials. Anhydrous ethyl ether (EE) was purchased from Mallinkrodt Inc; and was used directly. Tetrahydrofuran (THF) was distilled from sodium-benzophenone ketyl. BCl_3 (1M solution in CH_2Cl_2), *t*-BuLi (1M solution in hexane) and triisopropyl borate were obtained from the Aldrich Chemical Co. Anhydrous $FeCl_3$ purchased from the Fisher Scientific Co. was used under N_2. Absolute ethanol obtained from the Midwest Grain Products Co. was used without purification. The chiral alkylboronic esters (**5-8**) used in this study were prepared in high enantiomeric purity according to the reported procedures.[19-21] diethyl (*E*)-1-hexenylboronate (**9**) [23] and diethyl (*Z*)-1-hexenylboronate (**10**) [24] were prepared according to the reported procedures. Phenylboronic acid from the Aldrich Chemical Co. was used as such and also converted into diethyl phenylboronate (**11**).

Preparation of Chiral Monoalkyl-, (*E*)- and (*Z*)-1-Hexenyl-, Phenyl- and *tert*-Butyldichloroboranes. The following procedure for the preparation of *n*-hexyldichloroborane is a representative. In a dry 100 mL reaction flask, equipped with a

rubber septum and a magnetic stirring bar, was placed 100 mg (3 mole %) of anhydrous $FeCl_3$ and 40 mL (40 mmol) of a 1M solution of BCl_3 in CH_2Cl_2 under static pressure of N_2. The reaction flask was cooled to 0 °C and 3.72 g (20 mmol) of diethyl *n*-hexylboronate[16] was slowly added in 10 min. The reaction mixture was stirred at 0 °C and 25 °C for 1h each. The progress of the reaction was monitored by ^{11}B NMR. After 2h the solvent was removed under reduced pressure (20 mm Hg) and the resulting residue was extracted with CH_2Cl_2 (3 x 40 mL). The extracts were combined together by means of a double ended needle and the solvent was removed under reduced pressure. The residual liquid on distillation under reduced pressure yielded a colorless liquid , 2.65 g (16 mmol, 80%) of *n*-hexyldichloroborane (2), bp 100 °C (100 mm Hg); lit.[17] bp 102-104 °C (102 mm Hg); ^{11}B NMR ($CDCl_3$): δ 63 ; ^1H NMR ($CDCl_3$): δ 0.90 (t, 3H), 1.20-1.45 (m, 8H), 1.50-1.60 (m, 2H).

(2*R*)-2-Butyldichloroborane (13). Yield 65% ; bp 54 °C (32 mm Hg); lit.[27] bp 99 °C (748 mm Hg); ^{11}B NMR ($CDCl_3$) : δ 64 ; ^1H NMR ($CDCl_3$) : δ 0.95 (t, 3H), 1.10 (d, 3H), 1.20-1.35 (m, 1H), 1.45-1.75 (2m, 2H).

[(2*S*)-3-Methyl-2-butyl]dichloroborane (14). Yield 60% ; bp 44 °C (20 mm Hg); lit.[26] bp 110-112 °C (746 mm Hg); ^{11}B NMR ($CDCl_3$): δ 64 ; ^1H NMR ($CDCl_3$): δ 0.95 (2d, 6H), 1.05 (d, 3H), 1.50 (m, 1H), 1.95 (m, 1H).

[(1*S*, 2*S*)-*trans*-2-Methylcyclopentyl]dichloroborane (15). Yield 64%; bp 95 °C (110 mm Hg); lit.[17] bp 94-96 °C (110 mm Hg); ^{11}B NMR ($CDCl_3$): δ 64; ^1H NMR($CDCl_3$): δ 1.10 (d, 3H), 1.22 (m, 1H), 1.50-2.00 (2m, 6H), 2.10 (m, 1H) and ^{13}C NMR($CDCl_3$): δ 20.8, 26.0, 30.6, 36.3, 39.6.

[(1*S*, 2*S*)-*trans*-2-Methylcyclohexyl]dichloroborane (16). Yield 65%; bp 90 °C (20 mm Hg); ^{11}B NMR ($CDCl_3$): δ 63, ^1H NMR ($CDCl_3$): δ 0.90 (d, 3H), 0.95 (m, 1H), 1.10-1.40 and 1.65-1.85 (2m, 9H), 1.60 (m, 1H) and ^{13}C NMR ($CDCl_3$): δ 23.0, 26.2, 28.0, 34.3, 35.2, 41.6.

(*E*)-1-Hexenyldichloroborane (17). Yield 75%; bp 104 °C (100 mm Hg), lit.[26] bp 66-68 °C (18 mm Hg); ^{11}B NMR ($CDCl_3$): δ 52; ^{1}H NMR ($CDCl_3$): δ 0.90 (t, 3H), 1.35 (m, 2H), 1.45 (m, 2H), 2.30 (m, 2H), 6.10 (d, 1H, J = 17 Hz), 7.20 (m, 1H) and ^{13}C NMR ($CDCl_3$): δ 13.8, 22.3, 29.8, 35.4, 165.5.

(*Z*)-1-Hexenyldichloroborane (18). Yield 72%; bp 100 °C (103 mm Hg); ^{11}B NMR ($CDCl_3$): δ 52; ^{1}H NMR ($CDCl_3$): δ 0.90 (t, 3H), 1.25-1.55 (m, 4H), 2.60 (m, 2H), 6.00 (d, 1H J = 14 Hz), 6.77 (m, 1H) and ^{13}C NMR ($CDCl_3$): δ 13.9, 22.4, 31.5, 33.5,163.7.

Phenyldichloroborane (19). Yield 67%; bp 66 °C (11 mm Hg); lit.[10b] bp 66-66.5 °C (11 mm Hg); ^{11}B NMR ($CDCl_3$): δ 55; ^{1}H NMR ($CDCl_3$): δ 7.50 (dd, 2H, *o*-H), 7.70 (dd, 1H, *p*-H), 8.20 (d, 2H, *m*-H) and ^{13}C NMR ($CDCl_3$): δ 128.1, 135.2, 137.0.

***tert*-Butyldichloroborane (20).** Yield 65%; bp 86 °C (744 mm Hg); lit.[27] bp 88 °C (744 mm Hg); ^{11}B NMR($CDCl_3$): δ 64; ^{1}H NMR ($CDCl_3$): δ 1.10 (s, 9H).

Acknowledgment. Financial support from the United States Office of Naval Research is gratefully acknowledged.

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Table I. Conversion of Representative Chiral Alkylboronates into the Chiral Alkyldichloroboranes.[a]

R*BCl_2[b] R*=	Yield, %[c]	bp,°C (mm Hg)	^{11}B NMR δ ppm	Config	%ee[f]
(*R*)-2-butyl (**12**)	65	54(32)	64	2R[d]	≥99
(*S*)-3-methyl-2-butyl (**13**)	60	44(20)	64	2S[e]	≥99
(1*S*, 2*S*)-*trans*-2-methylcyclopentyl (**14**)	64	95(100)	64	1S,2S[e]	≥99
(1*S*, 2*S*)-*trans*-2-methylcyclohexyl (**15**)	65	90(20)	63	1S,2S[e]	≥99

[a]All reactions were carried out on 20 mmol scale. [b] The purity of R*BCl_2 was checked by ethanolysis and analysing the resulting boronic esters by ^{1}H NMR.[20b] [c] The isolated yields of the distilled products. [d] Reference 21d. [e] Reference 20b. [f] Enantiomeric and stereochemical purities were determined by capillary GC analysis of MTPA derivatives of alcohols derived by alkaline peroxide oxidation.

Table II. Conversion of Representative Alkyl-, (*E*)- and (*Z*)-1-Alkenyl-, and Arylboronates into the Corresponding Organyldichloroboranes.[a]

$RBCl_2$[b] R=	Yield, %[c]	bp,°C (mm Hg)	^{11}B NMR[d] δ ppm
n-hexyl- (**2**)	83	100(100)	63
tert-butyl- (**20**)	65	86(744)	64
(*E*)-1-hexenyl- (**17**)	75	104(100)	52
(*Z*)-1-hexenyl- (**18**)	72	100(103)	52
phenyl- (**19**)	67	66(11)	55

[a] All reactions were carried out on 20 mmol scale. [b] The purity of $RBCl_2$ was checked by ethanolysis and analysing the resulting boronic esters by ^1H NMR. [c] The isolated yields of the distilled products. [d] ^{11}B NMR were recorded in $CDCl_3$.